8EHQ-96-13602
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FERRO

8EHQ-0396-13602S

FERRO CORPORATION
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CLEVELAND, OHIO 44101
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FAX: (216) 441-4330

CERTIFIED MAIL - RETURN RECEIPT REQUESTED

March 6, 1996

A

Document Processing Center (TS-790)
Attn: Section 8(e) Coordinator
Office of Toxic Substances
U. S. Environmental Protection Agency
401 "M" Street, S.W.
Washington, D.C. 20460

SANITIZED COPY

ATTACHMENTS CONTAIN CONFIDENTIAL INFORMATION

RECEIVED
OPPT NCIC
96 MAR 11 AM 9:10

Dear TSCA Section 8(e) Coordinator:

This letter is being sent to you pursuant to Section 8(e) of the Toxic Substances Control Act (TSCA) to inform you in a timely manner of new information from a laboratory analytical test involving one of Ferro's products. Based on the laboratory test results, Benzene (CAS number 71-43-2) is believed to be formed from the decomposition of a minor component of a powder coating product during the curing (baking) step. This component, Triphenyl Tin Hydroxide (CAS number 76-87-9), has been added only to a few of Ferro's powder coating line products. The supplier of this component, Triphenyl Tin Hydroxide (or TPTH), does not mention this possibility in their MSDS. Our literature search has found no reference noting Benzene release from thermal decomposition of TPTH.

Ferro Corporation has been in the powder coating manufacturing business for more than 20 years and has been very active with customers and the Powder Coatings Institute in developing safe handling recommendations and practices for a variety of different types of organic powder coating product lines. In general, the use of powder coatings has vastly reduced the hazards to people and the environment that are associated with solvent based coating products. It is also well known in the industry that there can be small amounts of a variety of organic vapors released during the curing process. Our MSDS for these products, including those for products containing TPTH, mention the possibility of small amounts of toxic decomposition products being released and recommend the use of properly ventilated curing ovens.

The laboratory test was completed at Ferro's Technical Center laboratory. A sample of a TPTH containing powder coating product was heated in a closed container to a temperature to simulate a curing temperature (110°C for 20 minutes). A head space analysis of the vapors released found that Benzene was evolved from the product. Testing of the individual components that make up the product mixture has revealed that Triphenyl Tin Hydroxide (TPTH) decomposes to release Benzene.

Industrial hygiene studies conducted during lab procedures involving TPTH containing

RECEIVED 3/16/96

products have found no measurable Benzene levels in workplace air to date. Further testing at our Technical Center laboratory is indicating that the release of the Benzene from the powder coating product occurs at a rate that is temperature dependent. We also believe that the degree of cross-linking from the curing powder coating is also a factor in the rate of Benzene release. The low TPTH concentration, the relatively slow release rate and the short heating cycles during extrusion (<2 minutes) and curing (<30 minutes) explain the lack of detectable levels in the laboratory and would minimize potential levels in the commercial application of these powder coating products in ovens that are properly ventilated. Most, if not all, of the Benzene released would enter the exhaust gases from the curing oven and be safely removed from the building.

Ferro is not currently manufacturing TPTH containing products and has no plans to formulate new products with TPTH at this time. We are still evaluating this information and will be reviewing the status of any residual TPTH containing samples and product still at Ferro to ensure its responsible and appropriate handling. Ferro has also verbally notified the one customer laboratory that has a small quantity of TPTH containing powder coating product of this potential hazard and is sending them a revised MSDS.

For further information, please contact this writer at the letterhead address or telephone number.

Sincerely,

David A Wilson

David A. Wilson, CIH
Manager, Occupational
Safety and Health

ATTACHMENTS :

1. Benzene evolution test report of 2/14/96
2. Benzene evolution test report of 3/4/96
3. Charcoal tube Benzene Monitoring Report of 3/4/96
4. Benzene Detector Tube Monitoring Report of 3/4/96
5. Confidentiality Substantiation Page

FERRO

INTEROFFICE CORRESPONDENCE

TO: Bob Van Amburgh — Powder Coatings

FROM: Robert Huff, Thomas Connors — Technical Center

DATE: February 14, 1996

SUBJECT: Benzene Levels in Powder Clearcoat

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[redacted] reported that a substantial amount ([redacted] by weight) of benzene was evolving from a submitted powder clear coat. In response to this, two samples were submitted for the determination of evolved benzene levels. Since it was assumed that any benzene evolved had to come from the [redacted] TPTH, one of the samples was formulated without TPTH.

Gas Chromatography/mass spectrometry (GC/MS) was first used to determine whether benzene was indeed being evolved from the powder coat. Using [redacted] procedure, samples were heated at 110°C for twenty minutes and then injected into the GC/MS. The results showed that benzene was evolving from the powder coat with TPTH (PC702-82-2), and no benzene was observed evolving from the sample with no added TPTH (PC702-82-1). Benzene was also observed evolving from a sample of TPTH alone which was heated under the same conditions as above.

The amount of benzene evolving from PC702-82-2 was determined using our automatic headspace sampler coupled with an HP5890 GC equipped with an FID detector. The method used for quantitation was a multiple headspace extraction (MHE) method as described by Kolb[1]. The results found [redacted] by weight of benzene evolving from the powder coat. It should be noted that there are some assumptions implied in quantitation by MHE, mainly that the degradation of TPTH was complete in the twenty minutes of heating prior to injection and additional work is needed to clear up these problems. Nonetheless, substantial amounts of benzene does evolve from the powder coat.

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[1] B. Kolb, Chromatographia, 15(9), 587-594(1982)

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Conclusions:

1. Substantial amounts [redacted] by weight) of benzene evolves from the powder clear coat.

2. Benzene evolution is due to TPTH.

3. Benzene is evolved upon heating TPTH by itself.

Robert Huff

Thomas Connors

cc: S. Miller, E. Corcoran, E. White, ATS# 70-00-1-140-00, CHR959

FERRO

INTEROFFICE CORRESPONDENCE

CONFIDENTIAL

TO: Susan Miller — Powder Coatings

FROM: Robert Huff — Technical Center

DATE: March 4, 1996

SUBJECT: Benzene Evolution from TriphenylTin Hydroxide

A previous report confirmed reports that benzene evolves from powder clearcoat PC702-82-2 upon heating. The report also determined that the benzene evolution was a decomposition product of TriphenylTin Hydroxide (TPTH), and that, after 20 minutes at 110°C, [redacted] benzene by weight evolved from the powder coating as calculated by a multiple headspace extraction method. Additional work was then requested in three areas. The first, was to determine the amount of residual benzene in the TPTH. Secondly, to examine the TGA curves of TPTH heated under both nitrogen and air atmospheres. Lastly, work was requested to study benzene evolution over time at both 110°C and 145°C.

Since it was desirable to not heat the TPTH, the analysis of residual benzene was determined by HPLC. A sample of TPTH was slurried in a known amount of acetonitrile, and a filtered aliquot of this solution was injected onto a C18 column and the benzene was eluted under isocratic conditions. The amount of residual benzene was determined to be less than 0.01% by weight of TPTH.

Attached are the thermograms from the TGA analysis of TPTH under nitrogen and air atmospheres. The thermograms are almost identical up until 333°C where the sample in air gains a little weight presumably due to uptake of O_2. The percent weight losses and temperatures at the weight loss inflection points agree very well with those reported by Donaldson[1]. It should be noted that Donaldson does not report the evolution of benzene and that the TGAs show very little weight loss in the 100°C to 190°C range.

Headspace evolution of benzene over time in the clearcoat was monitored at 110°C and 145°C. To carry out this experiment, vials containing [redacted] of the clearcoat were placed in the headspace sampler, and the vials were sampled at 6.75 minute intervals. Attached is a graph showing the micrograms of benzene evolving over time for the two temperatures. Note that benzene is continuously evolved from the powder coat for the first hour. This means that the method used to calculate benzene evolution in

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the previous report was in error. The benzene evolution curves become asymptotic after approximately an hour, and the amount of benzene evolved at 110°C and 145°C approach [redacted] and [redacted], respectively. The amount of benzene evolved at 145°C in the first 2 minutes of heating was 0.02%.

The headspace data appears at first glance to contradict the TGA data which shows that between 110°C and 190°C (an 8 minute interval at a 10°C/minute heating ramp) very little weight is lost while one would estimate at least a 5% TGA weight loss from the headspace data. This probably is due to differences in the decomposition mechanisms between the pure material and a very dilute, finely dispersed amount of material in the powder coat. The two methods used in heating the samples may also be a factor since Donaldson himself reported significantly different decomposition products depending on whether TPTH was heated stepwise or directly.

Conclusions:

1. The amount of residual benzene in TPTH was less than 0.01%.

2. At both 110°C and 145°C, benzene is continuously evolved over the first hour.

3. The amount of benzene evolution reported previously was in error. Benzene evolution at 110°C and 145°C approaches [redacted] and [redacted], respectively. The amount of benzene evolved at [redacted] in the first 2 minutes of heating was 0.02%.

4. There are no significant differences in the TGA thermograms run under air and nitrogen atmospheres.

[1] J.D. Donaldson et al, Polyhedron 4(7), 1293-5, 1985

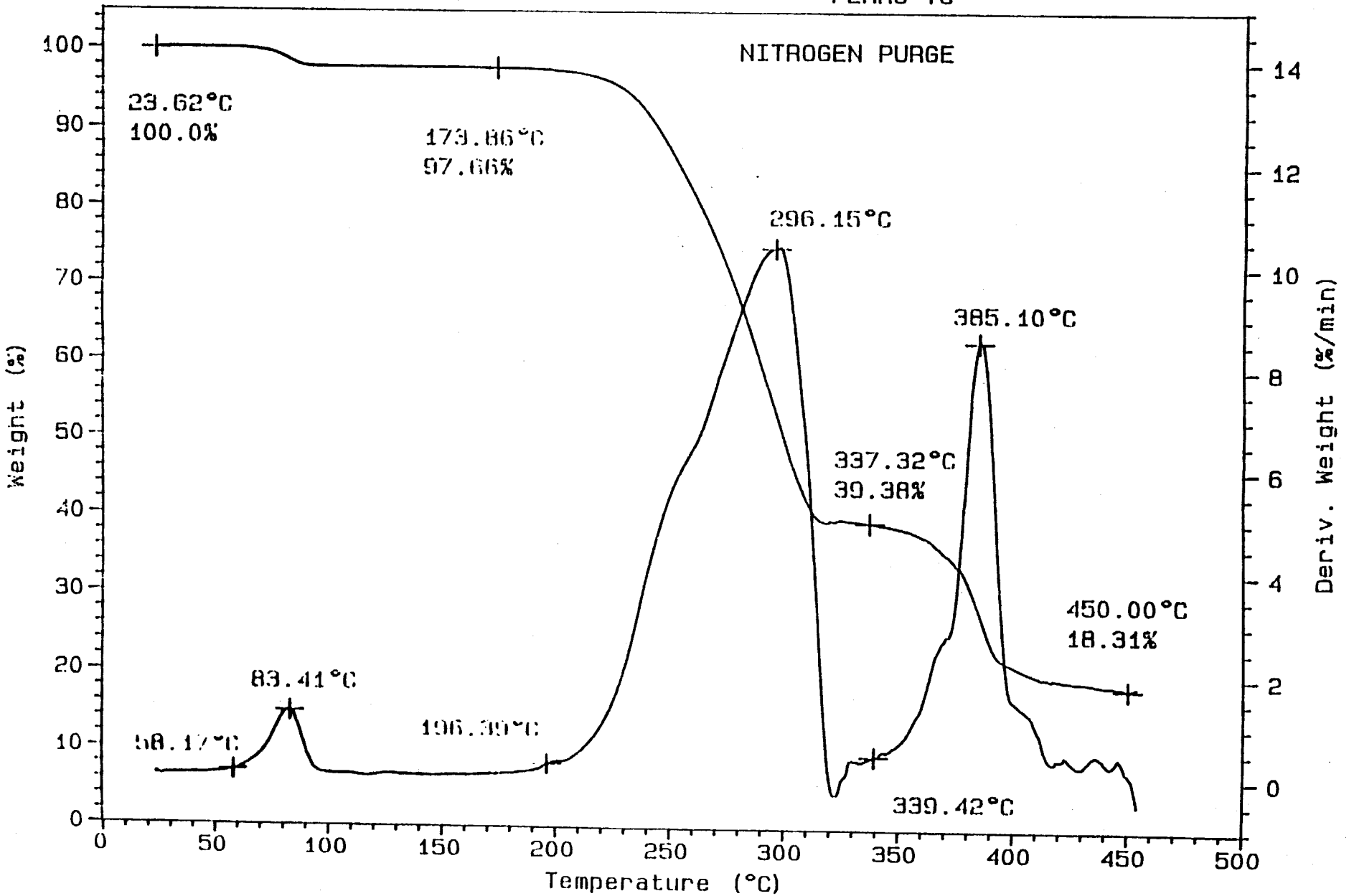
Robert Huff

cc: D. Wilson, J. Verdone, E. Corcoran, T. Connors, E. White, ATS# 70-00-1-140-00, CHR979

Sample: TPTH RM 366
Size: 25.0684 mg
Method: TGA 10°C/MINUTE
Comment: N2 PURGE, 10°C/min

TGA

File: TGA-0272.01
Operator: M.R.Mack
Run Date: 27-Feb-96 13:08
FERRO TC

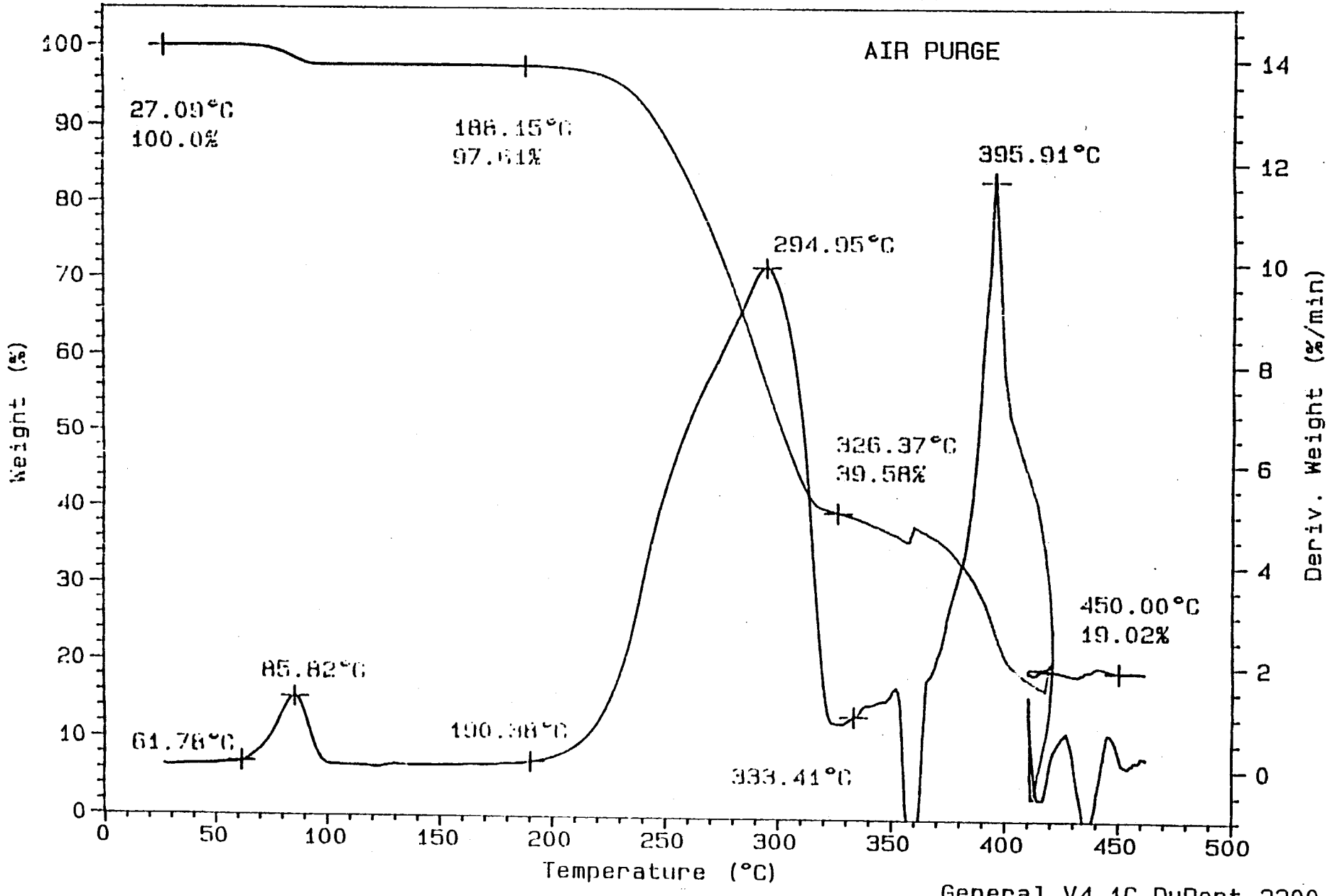


General V4.1C DuPont 2200

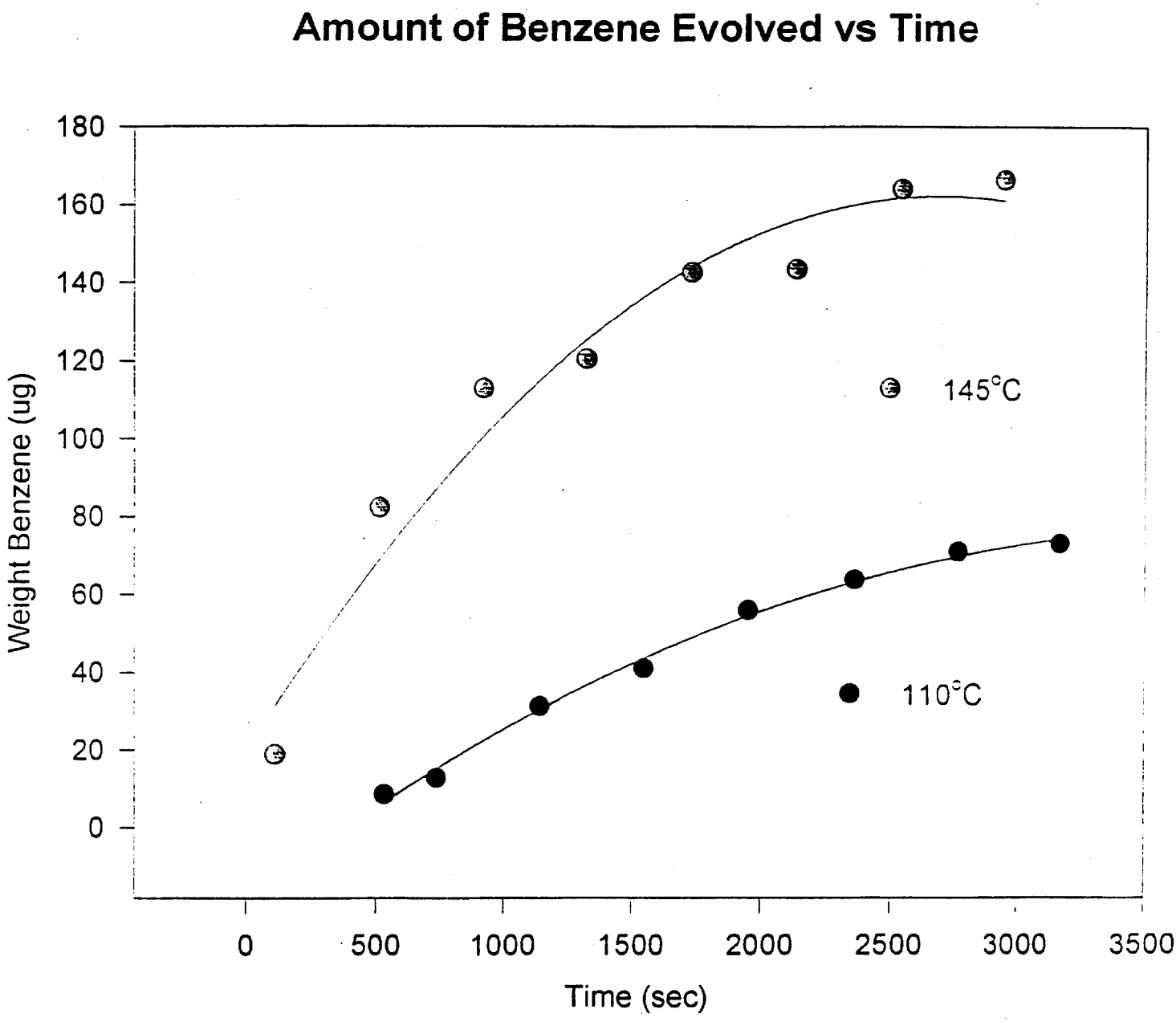
Sample: TPTH AM 366
Size: 27.8615 mg
Method: TGA 10°C/MINUTE
Comment: AIR PURGE, 10°C/min

TGA

File: TGA-0273.01
Operator: M.A.Mack
Run Date: 27-Feb-96 14:21
FERRO TC



General V4.1C DuPont 2200


Amount of Benzene Evolved vs Time
Weight Benzene (ug)
180
160
140
120
100
80
60
40
20
0
0
500
1000
1500
2000
2500
3000
3500
Time (sec)
145°C
110°C

FERRO

CORPORATE ENVIRONMENTAL AFFAIRS DEPARTMENT

INTEROFFICE MEMORANDUM

Date: March 4, 1996

To: Carlos Ortiz - 02

From: Dave Wilson - 92

Subject: Charcoal Tube Monitoring for Benzene/Corrected Results

Attached is the corrected summary table of the results from my February 26th Benzene monitoring survey at the 4150 Powder Coating Lab. I had incorrectly read the sample analysis reports and listed <1 ppm on the first summary table for all samples when they should have been <0.2 ppm which is even lower. This provides even better support and agreement with the detector tube monitoring where Joe Verdone found no measurable color change in the tubes that could be attributed to benzene. The detection limit for the detector tubes is 0.25 ppm.

These results should be considered worst case for the extrusion step since the exhaust ventilation for the extruder port was closed during this testing. However, the curing oven was was well ventilated which could have prevented any significant amounts of benzene from being released into the room and being detected.

Dave Wilson

cc: Ron Farrell
Sue Miller
Bob Van Amburgh
Joe Verdone
Bill Prior
Champ Bowden

Ferro Corporation
Industrial Hygiene Survey of Feb. 26, 1996 / Cleveland Powder Coatings Lab
Completed by David A. Wilson, CIH
Monitoring for Benzene using large charcoal tubes.
Analysis by Corning Industrial Labs, Youngstown, OH

CORRECTED REPORT
03/01/96

Sample	Activity	Start Time	Stop Time	Sample Time	Flow Rate	Total Volume	Benzene Concentration	Ventilation Controls
A *	Tube over extruder port, Werner/Phleiderer extruder, 4500 g, PC-702-75-1	2:19 PM	2:38 PM	19 min.	0.5 L/min	9.5 Liters	<0.2 ppm	Vent hood over extruder port turned off.
B *	Tube under extruder rolls where lab tech sits to guide material into container**	2:21 PM	2:39 PM	18 min.	0.5 L/min	9.0 Liters	<0.2 ppm	Vent hood over extruder port turned off.
E	Tube over extruder port, Werner/Phleiderer extruder.	2:38 PM	2:54 PM	16 min.	0.5 L/min	8.0 Liters	<0.2 ppm	Vent hood over extruder port turned off.
F	Tube under extruder rolls where lab tech sits to guide material into container**	2:39 PM	2:55 PM	16 min.	0.5 L/min	8.0 Liters	<0.2 ppm	Vent hood over extruder port turned off.
C	Tube above oven &near exhaust, curing 12 panels of same material as above	3:42 PM	4:10 PM	28 min.	0.5 L/min	14 Liters	<0.2 ppm	Normal oven exhaust Spray booth exhaust left on
D	Tube between oven & spray booth where employee works (same panels as in Sa. C	3:43 PM	4:12 PM	29 min.	0.5 L/min	14.5 Liters	<0.2 ppm	Normal oven exhaust Spray booth exhaust left on
Blank	-------	-----	-----	----	----	----	<5 ug/sample	-------

* extruder barrel was too hot so feed was quickly shut down and most of the batch was run during samples E & F.
** employee wore organic vapor respirator since extruder port exhaust vent was closed.

OSHA Permissible Exposure Limit (PEL): 29CFR1910.1028
Benzene - 1 ppm, 8hr TWA

FERRO CORPORATION
POWDER COATINGS DIVISION

AIR SAMPLING RESULTS

BENZENE
CAS # 71-43-2

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DATE MONITORED: February 26, 1996
LOCATION: R & D Laboratory, Cleveland
AIR SAMPLING DEVICE: Gastec Model 400 pump
Sensidyne analyzer tubes: Benzene, part # 121SL, lot #50637
Minimim detectable concentration: 0.25 ppm

SAMPLE #1: GMA extruder room
Werner-Pfleiderer extruder
Extruding conditions: barrel zone #1 [redacted]
zone #2 [redacted]
Formulation: PC-702-75-1, contains [redacted] triphenyltin hydroxide

Sampled at end of barrel, at point of extrudate drop.
Note: Vent above end of barrel closed during sampling.
Operator wore organic vapor respirator.

Result: No benzene detected.
Note: some (5mm) color change to reddish brown in primary tube.

SAMPLE #2: Curing oven
Spray room #1
Product: PC-702-82-2
Cure schedule: 30 min. at 300°F

1. Sampled near oven exhaust (door side).
   Result: No benzene detected
   Note: slight discoloration band moved through measurement range

2. Sampled near oven exhaust (spray booth/controls side)
   Result: No benzene detected
   Note: slight discoloration band moved through measurement range.

Joe Verbon 3/4/96

Attachment to Ferro Corporation (Ferro) TSCA 8(e) Notice of March 6, 1996.

Substantiation for the Confidentiality Claim.

1. Specific customer names, ingredient concentrations and processing conditions as noted in this TSCA 8(e) notice should be treated as confidential, permanently. We do not anticipate a change in the market for this type of product that would decrease the harmful effects of disclosure. Although this particular formula will not be continued, this technology is directly transferrable to other viable products that Ferro is developing.

2. To Ferro's knowledge, there have been no other confidentiality determinations made by the U.S. EPA, other Federal agencies, or the courts in connection with this information.

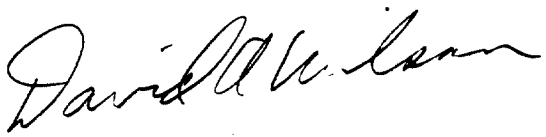
3. Ferro has not disclosed and has no plans to disclose this confidential information to its competitors or any other individuals outside the company. Ferro will not disclose this confidential information to its competitors or any other individuals outside the company in the absence of a written confidentiality agreement.

4. Ferro employees having knowledge of this confidential information are under confidentiality obligations to Ferro. Access to this information is limited to those Ferro employees and contractors whose duties require their having this information. Our facilities are not open to the public where this confidential information may be available. Any employee or non-employee of Ferro who is not under specific confidentiality obligation is denied access to any location within the facility where confidential information may be disclosed. All prospective publications which may disclose confidential information are reviewed by an attorney to delete any such information prior to publication.

5. The confidential information as designated in this notice does not appear and is not referred to in any advertising or promotional literature, material safety data sheets for related products, professional or trade publications, or any other media available to the public or to Ferro's competitors.

6. Disclosure of all or part of the specific chemical composition of the Ferro product(s) referenced in this notice would substantially impair the competitive position of Ferro by depriving Ferro the opportunity to recover research and acquisition expenditures associated with the development and marketing of this type of product. The development of a commercial product is a time consuming and expensive process. Publication of specific information on customers, ingredient concentrations, and processing conditions would disclose a basis for marketing and/or production of similar commercially useful products. This would serve to reduce or eliminate the research and development efforts of a competitor and would essentially deprive Ferro of its property based on the investment of research funds expended to develop this type of product.

7. The information claimed as confidential in this notice is not "health and safety data" pursuant to 40 CFR Part 2.306(3)(i).



Triage of 8(e) Submissions

Date sent to triage:_____ (NON-CAP) CAP

Submission number: 13602 A TSCA Inventory: (Y) N D

Study type (circle appropriate):

Group 1 - Gordon Cash (1 copy total)

ECO AQUATO

Group 2 - Ernie Falke (1 copy total)

ATOX SBTOX SEN w/NEUR

Group 3 -HERD (1 copy each)

STOX	CTOX	EPI	RTOX	GTOX
STOX/ONCO	CTOX/ONCO	IMMUNO	CYTO	NEUR

Other (FATE, EXPO, MET, etc.):_____

Notes:

☒ This is the **original** 8(e) submission; refile after triage evaluation.

☐ This **original** submission has been **split**; rejoin after triage evaluation.

☐ Other:

Photocopies Needed for Triage Evaluation

entire document: 0 1 2 3

front section and CECATS: 0 1 2 3

Initials:_____ **Date:**_____

This submission contains no triagible Data

CECATS DATA:
Submission # 8EHQ-0396-13602 (S) SEQ. A

CECATS\TRIAGE TRACKING DBASE ENTRY FORM

TYPE: (INT.) SUPP FLWP

SUBMITTER NAME: Ferro Corporation

SUB. DATE: 03/06/96 OTS DATE: 03/12/96 CSRAD DATE: 07/16/96

CHEMICAL NAME:

TPTH

CAS#
71-43-2
76-87-9

INFORMATION REQUESTED: FLWP DATE:
0501 NO INFO REQUESTED
0502 INFO REQUESTED (TECH)
0503 INFO REQUESTED (VOL ACTIONS)
0504 INFO REQUESTED (REPORTING RATIONALE)

DISPOSITION:
(0639) REFER TO CHEMICAL SCREENING
0678 CAP NOTICE

VOLUNTARY ACTIONS:
0401 NO ACTION REPORTED
(0402) STUDIES PLANNED/UNDERWAY
(0403) NOTIFICATION OF WORKER/OTHERS
(0404) LABEL/MSDS CHANGES
0405 PROCESS/HANDLING CHANGES
0406 APP/USE DISCONTINUED
0407 PRODUCTION DISCONTINUED
0408 CONFIDENTIAL

INFORMATION TYPE:		P	F	C
0201	ONCO (HUMAN)	01	02	04
0202	ONCO (ANIMAL)	01	02	04
0203	CELL TRANS (IN VITRO)	01	02	04
0204	MUTA (IN VITRO)	01	02	04
0205	MUTA (IN VIVO)	01	02	04
0206	REPRO/TERATO (HUMAN)	01	02	04
0207	REPRO/TERATO (ANIMAL)	01	02	04
0208	NEURO (HUMAN)	01	02	04
0209	NEURO (ANIMAL)	01	02	04
0210	ACUTE TOX. (HUMAN)	01	02	04
0211	CHR. TOX. (HUMAN)	01	02	04
0212	ACUTE TOX. (ANIMAL)	01	02	04
0213	SUB ACUTE TOX (ANIMAL)	01	02	04
0214	SUB CHRONIC TOX (ANIMAL)	01	02	04
0215	CHRONIC TOX (ANIMAL)	01	02	04

INFORMATION TYPE:		P	F	C
0216	EPI/CLIN	01	02	04
0217	HUMAN EXPOS (PROD CONTAM)	01	02	04
0218	HUMAN EXPOS (ACCIDENTAL)	01	02	04
0219	HUMAN EXPOS (MONITORING)	01	02	04
0220	ECO/AQUA TOX	01	02	04
0221	ENV. OCCC/REL/FATE	01	02	04
0222	EMER INCI OF ENV CONTAM	01	02	04
0223	RESPONSE REQEST DELAY	01	02	04
0224	PROD/COMP/CHEM ID	01	02	04
0225	REPORTING RATIONALE	01	02	04
0226	CONFIDENTIAL	01	02	04
0227	ALLERG (HUMAN)	01	02	04
0228	ALLERG (ANIMAL)	01	02	04
0239	METAB/PHARMACO (ANIMAL)	01	02	04
0240	METAB/PHARMACO (HUMAN)	01	02	04

INFORMATION TYPE:		P	F	C
0241	IMMUNO (ANIMAL)	01	02	04
0242	IMMUNO (HUMAN)	01	02	04
(0243)	CHEM/PHYS PROP	01	02	04
0244	CLASTO (IN VITRO)	01	02	04
0245	CLASTO (ANIMAL)	01	02	04
0246	CLASTO (HUMAN)	01	02	04
0247	DNA DAM/REPAIR	01	02	04
(0248)	PROD/USE/PROC	01	02	04
0251	MSDS	01	02	04
(0299)	OTHER Thermal Decomposition	01	02	04

TRIAGE DATA:

NON-CBI INVENTORY: (YES) NO IN TSCA INIT

ONGOING REVIEW: YES (DROP/REFER) NO (CONTINUE) REFER

SPECIES: N/A

TOXICOLOGICAL CONCERN: LOW MED HIGH

USE: powder coating

PRODUCTION:

CAS SR

COMMENTS: